

Zinc ion conducting polymer electrolytes based on oligomeric polyether/PVDF-HFP blends

Hui Ye, Jun John Xu*

Department of Materials Science and Engineering, Rutgers, the State University of New Jersey, Piscataway, NJ 08854, USA

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Abstract

Here we report novel zinc ion conducting polymer electrolytes based on oligomeric polyether/PVDF-HFP blends with or without the incorporation of a small amount of organic carbonates. Their thermal properties, ionic conductivity and electrochemical properties are characterized and the effect of different Zn salts and incorporation of a small amount of organic carbonates are investigated. These polymer electrolyte membranes exhibit essentially no or very low volatility, high thermal stability, high ionic conductivity, wide electrochemical stability window, acceptable interfacial resistance with zinc, and the capability for reversible Zn plating/stripping. Particularly promising are electrolyte systems based on the combination of low lattice energy zinc imide salt and a special co-solvent of oligomeric poly(ethylene glycol) dimethyl ether (PEGDME) mixed with a small amount of ethylene carbonate (EC), dimensionally stabilized with PVDF-HFP. Such novel polymer electrolyte membranes could lead to the development of new kinds of electrochemical energy storage devices based on zinc electrochemistry, including solid-state, thin-film rechargeable zinc/air cells envisaged.

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1. Introduction

Zinc electrochemistry has been prominent in energy storage, as evidenced by the extensive use of the zinc/manganese dioxide alkaline batteries in the past few decades for a very wide variety of consumer applications and zinc/air batteries for hearing aids. Other zinc-based systems such as nickel–zinc (zinc/nickel oxyhydroxide), zinc/silver oxide, zinc/mercury oxide and zinc/bromine batteries also have their own application niches or targets [1]. Despite the fact that zinc-based batteries have been around for a long time, various zinc-based systems, including some rechargeable ones, have been under significant and increasing R&D efforts in recent years. This is largely due to both the high promise, yet to be fully realized, of zinc-based chemistries and the driving forces from the consumer electronics market, development of hybrid and electric vehicles and special applications including military applications [2]. Particularly noteworthy are zinc/air systems. Besides being the dominant choice for the power source for hearing aids [1], zinc/air systems are under active development for electric buses

and other electric vehicles and such systems have been referred to as zinc–air fuel cells [2]. The high theoretical energy density of zinc/air batteries, on both gravimetric and volumetric bases, along with their low cost, is also very attractive to both consumer electronics applications and special applications such as military applications.

The electrolyte used in zinc-based batteries has been predominantly aqueous alkaline electrolytes. This choice of electrolyte, despite the varying degrees of success it has achieved with various zinc-based chemistries, poses some serious limitations. As we recently discussed [3], in the case of zinc/air batteries, these limitations include the necessity of limiting the area for air access and mass transport rate in the air cathode due to concerns of electrolyte evaporation or ambient moisture uptake, degradation of performance due to electrolyte carbonation, and limited operating temperature range. Moreover, among other factors, the fact that thermodynamics dictates that recharging a zinc/air pair in an aqueous electrolyte is fundamentally unfavorable (since the OCV of the cell, 1.65 V, is higher than the stability window of the aqueous electrolyte, 1.23 V) and rechargeability would only be possible owing to kinetic factors (i.e., the large overpotentials associated with splitting of water), renders it very difficult to realize rechargeable aqueous electrolyte zinc/air cells with a long cycle life.

* Corresponding author. Tel.: +1 732 445 5606; fax: +1 732 445 3258.
E-mail address: johnxu@rci.rutgers.edu (J.J. Xu).

We have envisaged solid-state, thin-film zinc/air batteries based on zinc ion conducting non-aqueous polymer electrolytes [3]. Such systems would be expected to offer various advantages over current zinc/air batteries based on aqueous electrolytes, such as higher rate and power capabilities, a greater proportion of the theoretical energy density extracted at practical rates, increased shelf-life, wider operating temperature range and electrical rechargeability [3]. The development of such systems rests largely on the availability of zinc ion conducting solid polymer electrolytes with high ionic conductivity and other desirable properties, including, very importantly, non-volatility or at least very low volatility since zinc/air batteries are open to the ambient air during usage. Availability of such zinc ion conducting polymer electrolytes would enable development of other new kinds of zinc-based batteries as well. However, zinc ion conducting polymer electrolytes reported in the literature do not meet the basic and essential requirements for developing such zinc-air systems. Solid polymer electrolytes of PEO–ZnX₂ complexes, where PEO is high-molecular-weight poly(ethylene oxide) and X = Cl, Br, I, ClO₄, and CF₃SO₃, exhibit conductivities around 10⁻⁶ S cm⁻¹ over 60 °C, too low for application in batteries [4–7]. Polymer gel electrolytes swollen with aprotic solvents such as propylene carbonate (PC), ethylene carbonate (EC) and dimethylsulfoxide (DMSO) with zinc triflate (Zn(CF₃SO₃)₂) dissolved in them, were reported to exhibit high ionic conductivities on the order of 10⁻³ S cm⁻¹ [8–12]. However, the incorporation of large amounts of organic solvents such as PC or EC leads to rapid solvent evaporation in open systems, which in turn leads to rapid degradation of the gel electrolyte system and loss of ionic conductivity [3,13]. Recently, we have reported novel zinc ion conducting polymer electrolytes based on non-volatile ionic liquids with zinc salts dissolved in them and blended with poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP). These zinc ion conducting polymer electrolyte membranes exhibit high ionic conductivity, non-volatility and other desirable properties for potential application in the solid-state, thin-film, rechargeable zinc/air cells envisaged and other zinc-based systems [3]. Here we report another series of zinc ion conducting polymer electrolytes, based on oligomeric polyether as the electrolyte solvent, blended and dimensionally stabilized with PVDF-HFP, with or without the incorporation of a small amount of ethylene carbonate.

Oligomeric polyethers, with molecular weight from a few hundred to a few thousand, are typically viscous liquids or waxy solids at room temperature. A prominent example of oligomeric polyethers as electrolyte solvents for potential battery applications is poly(ethylene glycol) dimethyl ethers (PEGDMEs), which are methyl capped short-chain PEO, and possess excellent thermal and chemical stability. For example, PEGDME250 (*M_w* = 250) has a melting point around -20 °C and boiling point >300 °C. Its vapor pressure is very low, as evidenced by the fact that it exhibits negligible weight loss even when subject to dynamic vacuum for 24 h. Oligomeric PEGDMEs have been used as solvent for lithium ion conducting electrolytes, and lithium polymer (gel) electrolytes based on them have been studied rather extensively due to the high solubility of lithium salts in them and their good compatibility with the

lithium metal anode [14–17]. We have reported novel lithium polymer electrolytes based on PEGDME/cross-linked PMMA blends prepared via in situ polymerization, for potential application in rechargeable lithium cells including lithium/air cells [17]. To the best of our knowledge, however, there has been no report on the use of oligomeric polyethers or PEGDMEs for zinc ion conducting electrolytes. At the same time, we have found that PEGDMEs possess unusually strong capabilities for dissolving large amounts of zinc salts. For example, the solubility of zinc triflate, Zn(CF₃SO₂)₂, is at least an order of magnitude higher in PEGDME250 than in propylene carbonate (PC), despite the fact that PC is one of the strongest organic solvents for dissolving inorganic salts owing to its high dielectric constant, high electron pair donicity and appreciable acceptor number [18]. We have also found that the combined use of a PEGDME solvent and a zinc salt with a very large anion, e.g., zinc bis(trifluoromethanesulfonyl)imide (abbreviated as Zn(TFSI)₂), Zn[N(SO₂CF₃)₂]₂, not only leads to high solubility, but also high ionic conductivity. Coupled with their very low vapor pressure and the fact that they blend exceptionally well with a range of polymers such as PVDF-HFP [19] and PMMA [17], PEGDMEs appear to be rather suitable solvents for developing zinc ion conducting polymer electrolytes for potential applications, especially for the solid-state, thin-film zinc/air cells envisaged. Furthermore, we have found that blending PEGDME with a small amount of ethylene carbonate has surprisingly large beneficial effects on the ionic conductivity and other electrochemical properties of zinc ion conducting polymer electrolytes based on them, without affecting the extremely low volatility nature of the electrolyte system. In this paper, a series of zinc ion conducting electrolyte systems are described, with PC, EC, PEGDME or their mixtures as the electrolyte solvent and zinc triflate or Zn(TFSI)₂ synthesized in our laboratory as the electrolyte salt, blended and dimensionally stabilized with PVDF-HFP. The prospect of developing zinc ion conducting polymer electrolytes based on PEGDME for our envisioned application is discussed.

2. Experimental

Zinc triflate (Zn(CF₃SO₂)₂), abbreviated as Zn(Tf)₂, zinc dust, trifluoromethanesulfonimide (HTFSI) and ethylene carbonate (EC) were purchased from Sigma–Aldrich. Poly(ethylene glycol) dimethyl ether (molecular weight = 250, referred to as PEGDME hereafter) were purchased from Sigma–Aldrich and dried under vacuum for 24 h before use. Battery grade propylene carbonates (PC) and co-solvent PC/EC (1:1, weight ratio) were purchased from Ferro Corporation and used as received. Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), KYNAR 2801, was kindly provided by ATOFINA Chemicals. Zn(Tf)₂ was dried under vacuum for 24 h at 110 °C prior to use. Zn(TFSI)₂ was synthesized by reaction of HTFSI with over-stoichiometric zinc dust [3,20].

The solubility of Zn salts in different solvents was determined by intermittently adding the salt to the solvent under continuous stirring until the solution became turbid. Co-solvents were obtained simply by mixing the individual solvents in appropriate

weight ratio and stirring overnight. Polymer electrolyte membranes were prepared by a solution casting method. A zinc electrolyte solution was prepared by dissolving a zinc salt in a solvent or co-solvent with desired concentration. PVDF-HFP was dissolved in acetone with a concentration of 7.5 wt%. The electrolyte solution was then mixed with the PVDF-HFP/acetone solution and a viscous mixture solution resulted. The weight ratio of the electrolyte solution to PVDF-HFP was fixed to be 7:3 throughout the study. The viscous mixture solution was cast over a Teflon tray and the acetone was evaporated and a freestanding membrane of 150–170 μm thickness resulted. All preparation steps were carried out in an argon-circulating glove box. The concentration of the electrolyte membranes refers to the molarity (M or mol l^{-1}) of the zinc salt in the corresponding liquid electrolyte solution, i.e., excluding the PVDF-HFP polymer.

Thermogravimetric analysis (TGA) of the membranes was performed with a Perkin-Elmer TGA7. The measurements were carried out from room temperature to 200 $^{\circ}\text{C}$ under flowing N_2 with a heating rate of 10 $^{\circ}\text{C min}^{-1}$. Differential scanning calorimetry (DSC) was performed with a Q1000 DSC system from TA Instruments, Inc. The measurements were carried out at the temperature range from -50 to 150 $^{\circ}\text{C}$ at a heating and cooling rate of 10 $^{\circ}\text{C min}^{-1}$. A cooling–heating–recooling cycle was carried out first and DSC data was collected during the subsequent, namely, the second heating step.

The ionic conductivity of liquid electrolyte solutions was measured by an Oaklon Conductivity Meter. The ionic conductivity of the polymer electrolyte membranes was determined by the AC Impedance method, using a Solartron 1287 Electrochemical Interface combined with a 1260 Impedance/Gain-phase Analyzer. The frequency range used for the impedance measurements was 1 MHz to 10 Hz and the amplitude used was 5 mV. The conductivity measurement set-up was assembled inside the glove box by sandwiching the polymer electrolyte membrane (12.7 mm in diameter and approximately 150 μm in thickness) between two stainless-steel discs and hermetically sealing the assembly inside a Hohsen Test Cell (Hohsen Corporation, Japan). The Test Cell was placed inside an environment chamber (B-M-A, Inc.), which provided temperature control, and the measurements were performed from -10 to 80 $^{\circ}\text{C}$. Cyclic voltammetry tests were carried out using a symmetric cell of Zn/membrane/Zn inside the glovebox. The interfacial resistance between the Zn electrode and the membrane was determined by performing AC Impedance analysis of the Zn/membrane/Zn cell, using a frequency range of 1 MHz to 0.01 Hz and amplitude of 5 mV. The electrochemical stability of the membranes was evaluated by means of linear potential sweep voltammetry using a similar cell inside the glovebox, in which a freshly polished stainless-steel disc was used as the working electrode and a Zn disc served as both the counter electrode and the reference electrode.

3. Results and discussion

Table 1 lists solubility data of $\text{Zn}(\text{Tf})_2$ and $\text{Zn}(\text{TFSI})_2$ in some organic solvents, PEGDME and their mixtures. The ionic con-

Table 1
Solubility of $\text{Zn}(\text{Tf})_2$ and $\text{Zn}(\text{TFSI})_2$ in different solvents and ionic conductivity of the electrolyte solutions (25 $^{\circ}\text{C}$)

Electrolyte solution	Solubility (mol l^{-1})	Ionic conductivity ($10^{-3} \text{ S cm}^{-1}$)
$\text{Zn}(\text{Tf})_2/\text{PC}$	0.04	0.72
$\text{Zn}(\text{Tf})_2/0.5\text{PC} + 0.5\text{EC}$	0.10	1.2
$\text{Zn}(\text{Tf})_2/\text{PEGDME}$	0.40	0.12
$\text{Zn}(\text{TFSI})_2/\text{PEGDME}$	>0.50	1.1 ^a
$\text{Zn}(\text{Tf})_2/0.5\text{PC} + 0.5\text{PEGDME}$	0.93	1.3 ^a
$\text{Zn}(\text{TFSI})_2/0.1\text{EC} + 0.9\text{PEGDME}$	>1.0	1.6 ^a

^a Ionic conductivity for 0.5 mol l^{-1} Zn salt solution. Other ionic conductivities are for the saturated solutions.

ductivities of the corresponding saturated electrolyte solutions or at a specified concentration are also listed. Note that the solubility of $\text{Zn}(\text{Tf})_2$ in PC and 0.5PC + 0.5EC (i.e., PC/EC mixture in 1:1 weight ratio) is only 0.04 and 0.1 M (mol l^{-1}), respectively, despite the fact that PC and EC are among the strongest organic solvents for dissolving organic salts. In fact, the discovery that lithium could be electrochemically deposited from a solution of LiClO_4 in PC and the electrolyte solution is relatively stable with lithium metal is credited for starting the area of lithium battery research [21]. PC and EC have ever since played very important roles as electrolyte solvents for lithium batteries, and lithium triflate in PC or PC/EC has been one of the most common electrolyte systems used in lithium battery research. The fact that zinc triflate or $\text{Zn}(\text{Tf})_2$ has dismally low solubility in PC or PC/EC underlines the difficulty of developing non-aqueous zinc electrolytes. The very low solubility may be understood in light of a few factors. Owing to the fact that the zinc ion is divalent, one mole of the zinc salt contains two moles of the monovalent anion compared with only one mole in the corresponding lithium salt. The lattice energy of one mole of the zinc salt should be significantly higher than that of one mole of the corresponding lithium salt. Moreover, the zinc salt is significantly more covalent in nature than the corresponding lithium salt and consequently is much more difficult to dissolve in polar solvents. Surprisingly, however, the solubility of $\text{Zn}(\text{Tf})_2$ in PEGDME is high and as much as 10 times that in PC, despite the fact that PEGDME's dielectric constant is much lower (7.88 for PEGDME compared with 65 for PC [22]) and it is significantly more viscous. The underlying reasons for PEGDME's unusual solvating capacity are not fully understood, although it apparently has to do with the high electron pair donicity of the polyethers, as with ethers. While solubility is certainly one of the first considerations when developing an electrolyte, it is the ionic conductivity that is more directly pertinent to electrochemical application. The ionic conductivity of the saturated $\text{Zn}(\text{Tf})_2/\text{PEGDME}$ solution is disappointingly low despite the high solubility, and it is lower than that of the saturated $\text{Zn}(\text{Tf})_2/\text{PC}$ solution or $\text{Zn}(\text{Tf})_2/(0.5\text{PC} + 0.5\text{EC})$ solution (Table 1). These data suggest different solvating mechanisms of the Zn salt in the highly polar solvent PC or PC/EC and in PEGDME. Not only do PC and EC have very high electron pair donicity (DN) hence strong capability for solvating cations, but

also their high polarity implies an appreciable acceptor number hence at least some capability for solvating the anions as well [18]. This suggests a relatively high percentage of free cations and anions and a low percentage of neutral ion pairs in the electrolyte solution for the amount of zinc salt that is dissolved, although the solubility is low due to the factors discussed above. The fact that the percentage of free ions is relatively high may also be explained by the high dielectric constant of the PC or PC/EC solvent, which significantly reduces the electrostatic forces between the ions. The relatively low viscosity of the PC or PC/EC solvent also helps ensure relatively high mobility of the free ions, as in such small-molecule solvents the ions migrate with their solvation sheath moving along with them and viscosity of the medium is a determining factor of their mobility [23]. On the other hand, polyethers such as PEGDME possess high electron pair donicity but very poor acceptor number. PEGDME dissolves the salt through forming complexes with the cations and the anions are basically un-solvated [24]. The electrostatic forces between the ions are therefore not as significantly reduced, a fact that can also be explained by the low dielectric constant of PEGDME. As a result, there must be a high percentage of neutral ion pairs, which have no contribution to the ionic conductivity, and a low percentage of free ions. The fact that ion migration in PEGDME is likely facilitated by the segmental motion of the oligomer chains, as in PEO, also points to relatively low ion mobility compared with that in small-molecule solvents.

One way to increase the ionic conductivity of PEGDME electrolytes would be to use zinc salts with larger anions. The electrical charge on larger anions is more delocalized, and as a result, the lattice energy of the salt is lower and the electrostatic force between the zinc cation and the anion in the electrolyte is weaker. These factors should lead to even higher solubility in PEGDME and higher percentage of free ions, hence higher ionic conductivity. Indeed, this has been realized with the $\text{Zn}(\text{TFSI})_2$ salt synthesized in our laboratory [3]. As shown in Table 1, $\text{Zn}(\text{TFSI})_2$ has even higher solubility in PEGDME than $\text{Zn}(\text{Tf})_2$. More importantly, the conductivity of 0.5 M $\text{Zn}(\text{TFSI})_2$ /PEGDME solution is an order of magnitude higher than that of the saturated $\text{Zn}(\text{Tf})_2$ solution, i.e., 0.4 M $\text{Zn}(\text{Tf})_2$ /PEGDME. The trifluoromethylsulfonyl imide ion (TFSI) is very large and polymer electrolytes based on LiTFSI have been rather extensively studied for lithium batteries [24,25]. Here the benefit of utilizing charge delocalization through such a large anion is demonstrated for the first time for a zinc polymer electrolyte, and the effect appears to be even more dramatic than with corresponding lithium polymer electrolytes.

Another way to increase the ionic conductivity and introduce other desirable properties would be through the approach of co-solvents, i.e., mixing of different solvents, which compensate for the drawbacks of each other leading to synergistic effects. This has been done extensively for lithium electrolytes based on organic solvents. In fact, the electrolytes used in commercial lithium ion batteries are based on solvent mixtures [26]. In our case for the zinc electrolytes, we have found that mixing PEGDME with PC or EC has surprisingly large beneficial effects. Comparing the solubility and conductivity data of

$\text{Zn}(\text{Tf})_2$ in PC, PEGDME, and 0.5PC + 0.5PEGDME (i.e., PC and PEGDME in 1:1 weight ratio) listed in Table 1, the advantage of co-solvents combining the high-dielectric-constant PC and the high-donicity PEGDME is evident. The solubility of $\text{Zn}(\text{Tf})_2$ in the 1:1 mixture is significantly higher than in either PEGDME or PC, and in fact is more than 2 times than in PEGDME alone and more than 20 times than in PC alone. The ionic conductivity is also significantly increased; in fact, it is an order of magnitude higher than that of the electrolyte based on PEGDME alone with the same salt and similar concentration. The rather dramatic effects of mixing PEGDME with PC may be explained by synergies between the two solvents. The combination of PEGDME's unusually strong capability for dissolving zinc salts and its low acceptor number and dielectric constant would lead to the formation of complexes with the zinc ions in large quantities but at the same time a high percentage of neutral ion pairs. With its appreciable acceptor number and high dielectric constant, PC would significantly promote the dissociation of the ion pairs so that the free ion concentration would be significantly increased. The strong capability of PEGDME for solvating the cations combined the appreciable capability of PC for solvating the anions would also lead to higher solubility. The plasticizing effect of PC would also lead to more rapid segmental motion of the oligomer chain, which in turn leads to enhanced ion mobility.

Incorporation of 50 wt% PC, however, gives rise to much increased volatility, which is detrimental to application in open systems such as the solid-state zinc/air batteries we envisioned. We attempted incorporating a small amount of EC into PEGDME and found that large beneficial effects also result but without increasing the volatility of the polymer electrolyte membranes based on the co-solvent, as described later. As seen in Table 1, the solubility of $\text{Zn}(\text{TFSI})_2$ in 0.1EC + 0.9PEGDME (i.e., mixture of EC and PEGDME in 1:9 weight ratio) is significantly higher than in pure PEGDME, and the ionic conductivity of the electrolyte based on the mixture is significantly higher than that based on pure PEGDME with the same salt and same concentration. In fact, the ionic conductivity of 0.5 M $\text{Zn}(\text{TFSI})_2$ /(0.1EC + 0.9PEGDME) reaches $1.6 \times 10^{-3} \text{ S cm}^{-1}$. This value is close to the conductivity of lithium ion conducting electrolytes based on mixtures of organic solvents and used in commercial lithium ion batteries [26], despite the fact that it is a zinc ion conducting electrolyte here and 90% of the electrolyte solvent is PEGDME, which has much higher viscosity than the organic solvents used in the lithium case. The conductivity achieved here is encouraging for potential applications and once again demonstrate the power of the co-solvent approach as well as the unusual properties of PEGDME as a solvent for the bivalent zinc salts.

Fig. 1 shows Arrhenius plots of the ionic conductivity of polymer (gel) electrolyte membranes formed by blending the electrolyte solutions listed in Table 1 with PVDF-HFP in 7:3 (electrolyte solution:PVDF-HFP) weight ratio. Table 2 lists their composition and sample number, along with room temperature conductivity, activation energy of the ionic conductivity, and interfacial resistance with zinc metal. The ionic conductivity of the membranes is a few to several times lower than that of the corresponding electrolyte solution. This is consistent with the

Table 2
Properties of the polymer (gel) electrolyte membranes

Polymer (gel) electrolyte	Sample no.	σ at 25 °C (10^{-3} S cm $^{-1}$)	Activation energy (kJ mol $^{-1}$)	Interfacial resistance (Ω)
0.04 M Zn(Tf) $_2$ /PC/PVDF-HFP	a	0.14	4.6	740
0.1 M Zn(Tf) $_2$ /0.5PC + 0.5EC/PVDF-HFP	b	0.22	5.0	239
0.4 M Zn(Tf) $_2$ /PEGDME/PVDF-HFP	c	0.03	10.0	1085
0.5 M Zn(TFSI) $_2$ /PEGDME/PVDF-HFP	d	0.17	9.6	469
0.5 M Zn(Tf) $_2$ /0.5PC + 0.5PEGDME/PVDF-HFP	e	0.20	10.5	298
0.5 M Zn(TFSI) $_2$ /0.1EC + 0.9PEGDME/PVDF-HFP	f	0.47	11.0	322

fact that PVDF-HFP is electrochemically inert in terms of ion solvation and its main role is to provide mechanical support and dimensional stabilization. It also suggests that the electrolyte solutions blend with the PVDF-HFP polymer likely at the molecular level, since the ionic conductivity would not be decreased to such an extent if the blending were at a microscopic rather than molecular level [15,27]. The excellent dimensional stability and mechanical properties observed of the membranes also suggest molecular level blending. An analysis of Fig. 1 shows that the ionic conductivity of the polymer (gel) electrolyte membranes exhibits a linear relationship between $\log \sigma$ versus T^{-1} above 40 °C and a downward curvature at lower temperatures. This behavior is similar to that of lithium ion conducting polymer (gel) electrolytes [24], which is related to the segmental motion of the polymer chain and is well described by the Vogel–Tammann–Fulcher (VTF) equation [28–30]:

$$\sigma = \sigma_0 \exp \left[\frac{-B}{(T - T_0)} \right]$$

As seen from Fig. 1, the ionic conductivity of the polymer gel electrolytes based on small-molecule organic solvents only, i.e., PC or PC/EC, exhibits weaker temperature dependence than that of the membranes containing PEGDME. Quantitatively, the activation energy of the ionic conductivity was calculated from the linear region of the $\log \sigma$ versus T^{-1} plots ($T \geq 40$ °C) and listed in Table 2. The activation energies of the polymer gel electrolytes based on PC or PC/EC are only about half of those of

the electrolyte membranes containing PEGDME. This supports our interpretation of the different solvation and transport mechanisms in these solvents. Ion transport in PEGDME or membranes based on PEGDME is expected to be facilitated by the thermally activated segmental motion of the polyether chain, the energy barrier of which is higher than that of thermally activated motion of small organic molecules owing to the fact that it is an oligomer, leading to higher activation energy. It is interesting to note that the activation energy of ion transport in membranes based on mixtures of PEGDME and PC or EC is about the same as that of membranes based on PEGDME only, and twice as much as that of membranes based on PC or PC + EC. This would suggest that ion transport in membranes based on mixtures of PEGDME and PC or EC is still largely facilitated by the segmental motion of the polyether chain, and the fact that the ionic conductivity is increased by the incorporation of PC or EC is through the plasticization effect in addition to increased ion dissociation. In terms of the magnitude of the ionic conductivity, the polymer (gel) electrolyte membranes listed in Table 2 follows the same trend as the corresponding liquid electrolyte solutions listed in Table 1, and the Zn(TFSI) $_2$ /0.1EC + 0.9PEGDME/PVDF-HFP membrane exhibits the highest ionic conductivity among all the membranes. It is 0.47×10^{-3} S cm $^{-1}$ at room temperature, above 1×10^{-3} S cm $^{-1}$ at 40 °C, and around 1×10^{-4} S cm $^{-1}$ at –10 °C. Such ionic conductivities for polymer electrolytes indicate promise for potential applications.

Thermal properties of the polymer (gel) electrolyte membranes were investigated by TGA and DSC. Fig. 2 shows the TGA curves of the membranes. Those based on PC or PC + EC

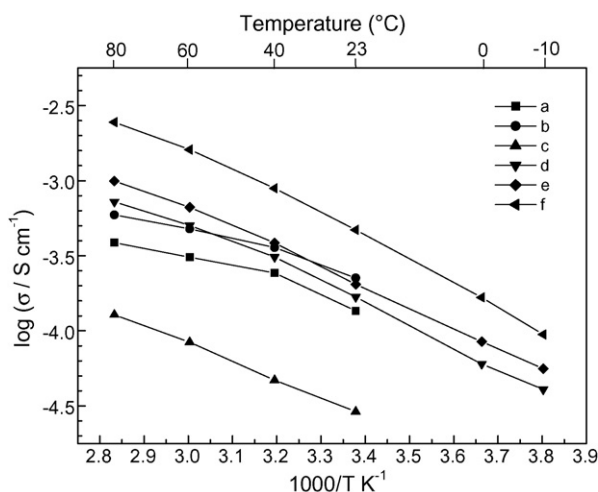


Fig. 1. Temperature dependence of the ionic conductivity of the polymer (gel) electrolyte membranes.

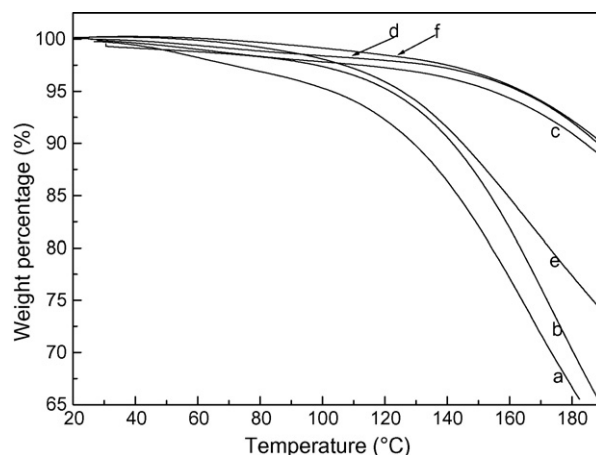


Fig. 2. TGA of the polymer (gel) electrolyte membranes.

only, samples a and b, exhibit large and rapid weight loss upon heating. The membrane based on 0.5PC + 0.5PEGDME, sample e, exhibits large and rapid weight loss as well. It has been reported that lithium polymer gel electrolytes incorporating large amounts of volatile organic solvents are not thermally stable and solvent evaporation occurs easily at elevated temperature [13]. The same phenomenon is observed here. We have also observed that these membranes visibly shrunk and lost their conductivity by half when left in an open environment inside the glovebox at room temperature for 3 days. The severe solvent evaporation is a concern even for application in sealed battery systems, and would render the electrolytes inapplicable for open systems such as the thin-film metal/air batteries envisaged. In contrast, the membranes based on PEGDME only, samples c and d, exhibit negligible weight loss up to 140 °C. The small weight loss below 140 °C likely resulted from residual acetone left in the membrane and moisture absorption during TGA sample preparation. It is interesting to note that the membrane based on 0.1EC + 0.9PEGDME, sample f, also exhibits negligible weight loss below 140 °C. Incorporation of the small amount of EC does not increase the volatility or degrade the thermal stability of the resultant electrolyte membrane, while significantly enhancing the solvating capability for zinc salts and the ionic conductivity, as described above, and enhancing other desirable electrochemical properties, as described below. These effects must be due to the synergistic interaction between EC and PEGDME at the molecular level, full elucidation of which must await further studies.

DSC measurements of the polymer (gel) electrolytes were performed in the temperature range from –50 to 150 °C (Fig. 3). It is found that the polymer (gel) electrolyte membranes exhibit single-phase behavior in a wide temperature range. Except for the membrane based on 0.5PC + 0.5EC, which shows an endothermic peak around 5 °C, all the other membranes shows no thermal event from –50 °C until a rather high temperature, where an endothermic peak appears which corresponds to the melting of the membrane. The melting point of the recast PVDF-HFP membrane is 139.5 °C [3]. Blending with the liquid components decreases the melting point to 83 °C for the mem-

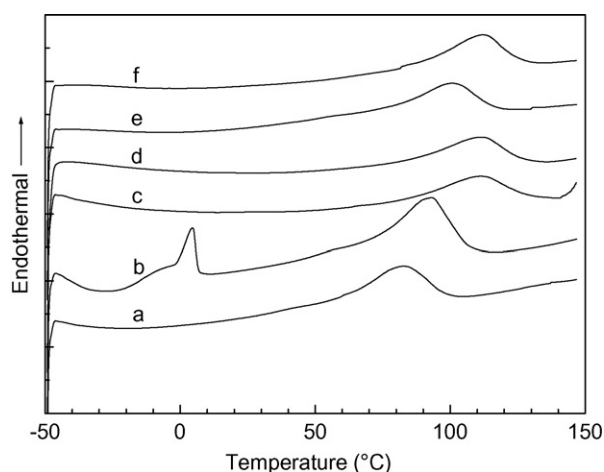


Fig. 3. DSC of the polymer (gel) electrolyte membranes.

brane based on PC, 92 °C for that based on 0.5PC + 0.5EC, and 101 °C for that based on 0.5PC + 0.5PEGDME. For membranes based on PEGDME or 0.1EC + 0.9PEGDME, this decrease of the melting point is less significant, consistent with the fact that PEGDME is a viscous oligomer. It is interesting to note that the melting point for the membrane based on 0.1EC + 0.9PEGDME, at 112 °C, is similar to those of the membranes based on PEGDME alone. It is significant that there is no thermal event in the membranes at the melting temperature of the individual solvents, PC, EC or PEGDME, whose melting point is around –48.8, 36.4 and –19.5 °C, respectively [19,31]. The blending of these solvents with PVDF-HFP must be at the molecular level to result in a highly homogeneous, largely amorphous phase where the only crystallinity present is the weak crystallinity of the recast PVDF-HFP [6], leading to only one melting point associated with the PVDF-HFP and no melting point associated with the individual solvents. The only exception is the membrane based on 0.5PC + 0.5EC. This may be due to the fact that this membrane is the only one with a large amount of EC whose melting point is very high at 36.4 °C [31]. At low temperatures around –50 °C, this electrolyte system would likely be semicrystalline, namely, there are EC-rich crystalline regions embedded in an otherwise largely amorphous gel phase. As the temperature rises, the crystalline regions melt leading to the endothermic peak at 5 °C. The fact that the membranes based on PEGDME or 0.1EC + 0.9PEGDME exhibit no discernible thermal transitions over a wide temperature range from –50 °C to around 110 °C is significant for their potential applications. The ability to operate in wide temperature ranges is important for many applications of advanced batteries. The single-phase nature of the polymer electrolyte membranes in wide temperature ranges, coupled with the fact that they exhibit negligible weight loss up to 140 °C (Fig. 2), gives rise to the possibility that their further optimization might enable operation of advanced batteries based on them in both exceptionally low and high temperature.

Fig. 4 shows cyclic voltammograms of symmetric Zn/membrane/Zn cells using the polymer (gel) electrolytes mem-

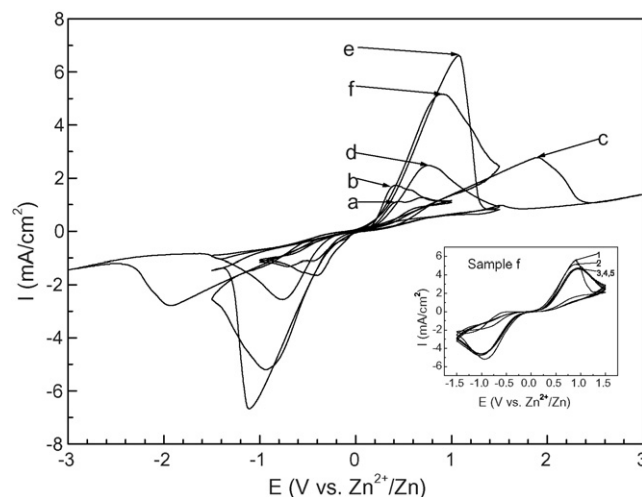


Fig. 4. Cyclic voltammograms of Zn/membrane/Zn symmetric cells using the polymer (gel) electrolyte membranes. Inset shows first five cycles with sample f. Scan rate = 10 mV s⁻¹.

branes. CV curve of the second cycle of samples a–f is shown, while the first five cycles of sample f are in the inset as a representative to show the reproducibility of the CV curves on multiple cycles. Reproducibility of CV curves on multiple cycles is similar for the other samples. Reversible zinc plating/stripping as shown in Fig. 4 indicates that Zn^{2+} ions are indeed mobile in the membranes and Zn is capable of dissolution into and deposition from the membranes, features that are essential for their potential application in zinc batteries. The peak current densities observed with the membranes based on PC and 0.5PC + 0.5EC (samples a and b) are low, 1.1 and 1.8 mA cm^{-2} , respectively, although the overpotentials associated with the peak current are relatively low. The membrane based on 0.4 M $\text{Zn}(\text{Tf})_2/\text{PEGDME}$ (sample c) gives rise to higher peak current densities, around 2.5 mA cm^{-2} , but the overpotentials are too high, which are attributable to the high resistivity of the membrane and the high interfacial resistance with zinc (see Table 1 and below). The membrane based on 0.5 M $\text{Zn}(\text{TFSI})_2/\text{PEGDME}$ (sample d) leads to a similar peak current density as sample c but much lower overpotentials, again demonstrating the advantage of using the zinc salt with a very large anion leading to much higher bulk ionic conductivity and also lower interfacial resistance with zinc (Table 1 and below). The cells using the membranes based on 0.5PC + 0.5PEGDME and 0.1EC + 0.9PEGDME (sample e and f) exhibit high peak current densities and moderate overpotentials, giving rise to the best overall performance and again demonstrating the advantage of the co-solvent approach and the synergistic effects between PC or EC and PEGDME. Comparing samples d and sample f, it is seen that incorporating 10 wt% EC leads to doubling the peak current density, which is likely due to higher concentration and mobility of Zn^{2+} ions in the electrolyte membrane as a result of the addition. These CV results also show that the cathodic stability limit of all the membranes is zinc deposition from the membranes.

Electrochemical impedance spectroscopy tests of the Zn/membrane/Zn cells were performed after five Zn plating/stripping cycles. The area of the Zn/membrane interface in the symmetrical cell was 1.98 cm^2 . The spectra of all samples from high to low frequency consist of a semi-circle followed by a sloping line. The spectrum of sample f is shown in Fig. 5 as a representative. The spectra can be interpreted by an equivalent circuit of a bulk resistance in series with a RC parallel and a diffusion component at low frequency. The RC parallel is associated with the Zn/membrane interface and the R is identified as the resistance of the interface. In fact, since there are two identical Zn/membrane interfaces in the symmetrical cell, the interfacial resistance is half of the value of the R as determined from the impedance spectrum, and listed in Table 2. The interfacial resistance associated with membranes based on PEGDME alone is high. Incorporating PC or EC can significantly decrease its value, another significant benefit of the co-solvent approach. The interfacial resistance must be a combination of the resistance associated with the kinetics of the two-electron transfer reaction of zinc (R_{kinetics}) and the resistance associated with any zinc surface film (R_{SEI}). It would be likely that a solid electrolyte interface (SEI) film forms at the surface of zinc, as in the case of lithium [32]. However, virtually nothing is known about

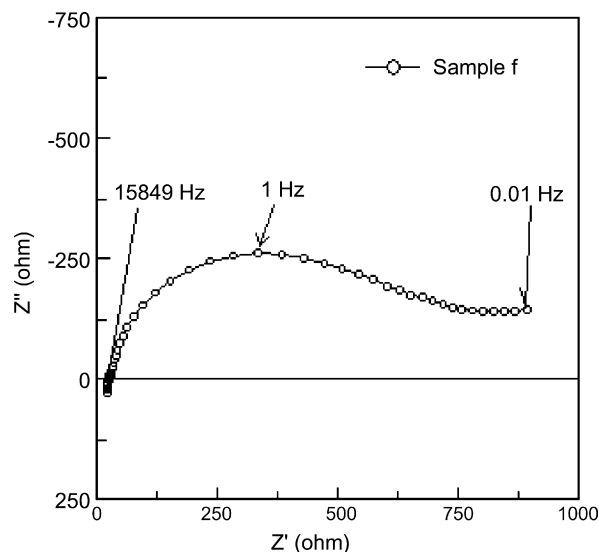


Fig. 5. Electrochemical impedance spectrum of the Zn/membrane/Zn cell (sample f), obtained after five Zn plating/stripping cycles.

the nature of such SEI films on zinc or the kinetics of the zinc electron transfer reaction in polymer electrolyte membranes, although it would be reasonable to expect that the resistance associated with the kinetics of the two-electron transfer reaction of zinc is significantly higher than that associated with the one-electron transfer reaction of lithium, while the SEI formation on zinc is not as severe as on lithium. In fact, by considering the values of the interfacial resistance listed in Table 2 and the zinc plating/stripping curves in Fig. 4, it may be concluded that the interfacial resistance should largely result from the slow kinetics of the two-electron transfer reaction of zinc and the contribution from the SEI film should be relatively small; namely, R_{kinetics} is large and R_{SEI} is small. Take sample f as an example. If the interfacial resistance was mostly due to R_{SEI} , which should not change significantly with the current density flowing through the interface, the potential of the Zn/membrane/Zn cell at the peak current in the CV test (Fig. 4) would be several volts, from a simple estimation of the voltage drop across the Zn/membrane interface (current times the interfacial resistance) and the ohmic drop of the voltage through the bulk resistance of the membrane. The fact that the cell voltage corresponding to the peak current is only ca. 0.75 V means that the voltage drop across the Zn/membrane interface cannot be estimated by the product of the current times the interfacial resistance as determined by AC impedance. AC impedance tests are performed under equilibrium conditions with a very small perturbation and the current flowing through the cell is minimal. The kinetics of the electron transfer reaction at the electrode/electrolyte interface is at the linear region and consequently the R_{kinetics} thus determined only applies to the linear region. At higher current densities, as in Fig. 4, the electron transfer reaction is at the Tafel region where the current density flowing through the interface varies exponentially, rather than linearly, with the voltage drop across the interface, and R_{kinetics} as determined by the AC impedance test under equilibrium conditions does not apply anymore. However, if the interfacial resistance as determined by the AC impedance

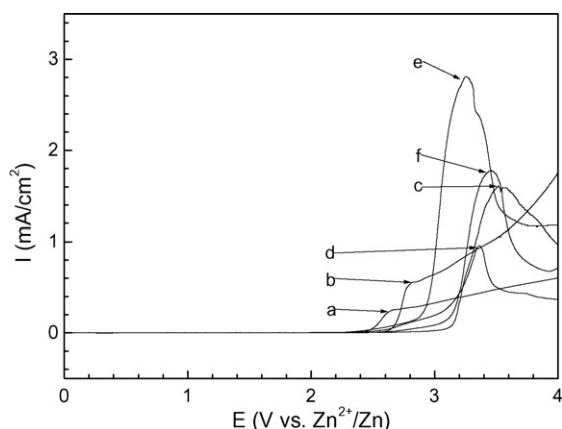


Fig. 6. Linear sweep voltammograms of the polymer (gel) electrolyte membranes using SS/membrane/Zn cells. Scan rate = 1 mV s^{-1} .

test were mostly due to R_{SEI} , then the voltage drop across the interface could be estimated by the product of the current times the interfacial resistance even at high current densities. These considerations point to the interfacial resistance as determined by AC impedance and listed in Table 2 being mostly due to R_{kinetics} , not R_{SEI} . They also suggest that the apparently high values of the interfacial resistance may not necessarily imply severe limitations on their application in Zn batteries. In fact, the peak current densities of zinc plating/stripping achievable in these membranes are relatively high at relatively low overpotentials (except sample c) (Fig. 4), although it would undoubtedly be beneficial for battery applications if the interfacial resistance, as well as the bulk resistance, could be reduced through further optimization.

To investigate the electrochemical stability of the polymer (gel) electrolyte membranes, linear sweep voltammetry was performed using SS/membrane/Zn cells with a slow scan rate of 1 mV s^{-1} . As shown in Fig. 6, the anodic stability limit of the membranes based on PC and 0.5PC+0.5EC (samples a and b) is 2.50 V and 2.65 V versus Zn^{2+}/Zn , respectively. Incorporating 50% PEGDME into the membrane based on PC can enhance the anodic stability to 2.8 V versus Zn^{2+}/Zn (sample e). The membranes based on PEGDME (samples c and d) or 0.1EC+0.9PEGDME have significantly higher anodic stabilities of over 3 V versus Zn^{2+}/Zn . It is interesting that incorporation of a small amount of EC into PEGDME even improves the anodic stability of the membrane to some degree, as seen from comparing samples d and f. The electrochemical stability windows of these membranes apparently are wide enough for potential application in zinc-based batteries such as zinc/air batteries whose open circuit potential is 1.65 V.

The results reported above demonstrate the promise of developing zinc ion conducting polymer electrolyte membranes based on oligomeric polyether/PVDF-HFP blends, and the advantages of using zinc salts with a very large anion and the advantage of incorporating a small amount of EC in PEGDME as electrolyte co-solvent. The membranes based on $\text{Zn}(\text{TFSI})_2$ in PEGDME or $\text{Zn}(\text{TFSI})_2$ in 0.1EC+0.9PEGDME are particularly promising, with their non-volatility, exceptional thermal stability in a wide temperature range, high ionic conductivity, wide electro-

chemical stability window, acceptable interfacial resistance with zinc, and the capability for reversible zinc plating/stripping. Further optimization of these membranes could lead to even more promising electrolyte systems for application in zinc batteries such as zinc/air batteries based on non-aqueous polymer electrolytes, which is currently underway.

4. Conclusion

In an attempt to develop zinc ion conducting polymer electrolyte systems for potential application in new kinds of zinc-based batteries especially non-aqueous zinc/air cells, a series of electrolyte membranes based on PC, EC, PEGDME and their mixtures, dimensionally stabilized by blending with PVDF-HFP, were investigated. It was found that PEGDME possesses unusually strong capability for solvating zinc salts. Zinc salts with a very large anion, such as $\text{Zn}(\text{TFSI})_2$, lead to not only high solubility in PEGDME, but also high ionic conductivity. Incorporation of a small amount of EC into PEGDME gives rise to surprisingly large beneficial effects in terms of zinc salt solubility, ionic conductivity and other electrochemical properties. Zinc electrolyte solutions based on these solvents blend well with PVDF-HFP, leading to polymer (gel) electrolyte membranes of a single-phase nature in a wide temperature range. However, those membranes based on PC or PC/EC mixture exhibit large weight loss in TGA tests or when left in an open environment, leading to rapid loss of ionic conductivity and rendering them inapplicable for open systems such as thin-film zinc/air batteries envisaged. The polymer electrolyte membranes based on PEGDME, or PEGDME with a small amount of EC incorporated, exhibit negligible weight loss up to 140°C . They also exhibit other desirable properties, including ionic conductivity on the order of $10^{-4} \text{ S cm}^{-1}$ at room temperature, a wide electrochemical stability window with the cathodic limit being zinc deposition and anodic limit greater than 3 V versus Zn^{2+}/Zn , acceptable interfacial resistance with zinc, and the capability for reversible zinc plating/stripping. They would be promising for applications in new kinds of zinc batteries based on non-aqueous or polymer electrolytes where non-volatility, high ionic conductivity and other favorable electrochemical properties of the electrolyte system are desired.

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